

AD-A114 868

CORNELL UNIV ITHACA SCHOOL OF CHEMICAL ENGINEERING F/G 7/4  
FUNDAMENTAL STUDIES OF THE STRUCTURE AND CHEMISTRY OF SOLID SUR--ETC(U)  
DEC 80 R P MERRILL AFOSR-80-0103

UNCLASSIFIED

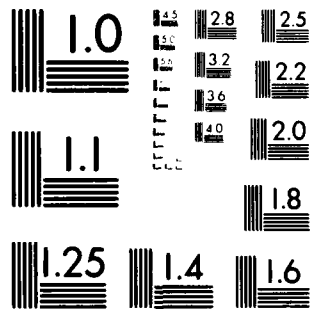
AFOSR-TR-82-0206

NL

1-1  
1-1



END  
DATE  
FILMED  
6 82  
DTIC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS 1963-A

AFOSR-TR- 32 -0206

*Fundamental Studies of the Structure and Chemistry of Solid Surfaces* (12)

FINAL REPORT

Dr. Robert P. Merrill

Cornell University  
School of Chemical Engineering

Ithac, New York 14853

AFOSR-80-0103

1 July 1977 - 31 December 1980

DTIC  
ELECTE  
MAY 26 1982  
H

DTIC FILE COPY

**DISTRIBUTION STATEMENT A**

Approved for public release  
Distribution Unlimited

Approved for public release  
Distribution Unlimited  
82 05 24 144

AD A114868

24 Feb 1982

# COMPLETED PROJECT SUMMARY

1. TITLE: Fundamental Studies of the Structure and Chemistry of Solid Surfaces
2. PRINCIPAL INVESTIGATOR: Dr. Robert P. Merrill  
H.F. Johnson Professor of Industrial Chemistry  
School of Chemical Engineering  
Cornell University  
Ithac, New York 14853
3. INCLUSIVE DATES: 1 July 1977 - 31 December 1980
4. GRANT NUMBER: AFOSR 80--0103
5. COSTS AND FY SOURCE: \$206,685, FY80
6. SENIOR RESEARCH PERSONNEL: Dr. Herbert Sawin
7. JUNIOR RESEARCH PERSONNEL:

Robert J. Purtell  
Karel K. Czanderna  
Suzan Miller

Masaharu Komiyama  
William Avrin  
Gar B. Hoflund

## 8. PUBLICATIONS:

"A Molecular View of Diffusion and Reaction in Porous Catalysts," R.P. Merrill, Journal of Catalysis, 50, 384 (1977).

"Broad-Frequency Chopper with Adjustable Duty Cycle," H.H. Sawin, D.D. Wilkinson, W.M. Chan, S.Smiriga and R.P. Merrill, J. Vac. Sci. Tech., 14, 1205 (1977).

"Reply to Comments of CFSO-BEBO Approach," R.P. Merrill and W.H. Weinberg, Journal of Catalysis, 51, 296 (1978).

"Double Rainbow Features in Classical Scattering from Solid Surfaces - Ne on Ag(111)," D.R. Dion, J.A. Barker, and R.P. Merrill, Chem. Phys. Let. 57, 117 (1980).

"Chemisorption and Reaction of NH<sub>3</sub> on Ni(111)," C.W. Seabury, T.N. Rhodin, R.J. Purtell, and R.P. Merrill, Surface Science, 93, 117 (1980).

AIR FORCE SCIENTIFIC RESEARCH (AFSC)  
NOTICE: TECHNICAL  
This technical report has been reviewed and is  
approved for release under E.O. 12958-12.  
Distribution is limited.  
MATTHEW J. [unclear]  
Chief, Technical Information Division

PUBLICATIONS (Continued):

"Adsorbate structures from Angle Resolved Photoemission:  $\text{NH}_3$  on Ir(111)," R.J. Purtell, R.P. Merrill, C.W. Seabury and T.N. Rhodin, Phys. Rev. Letters, 44, 1279 (1980).

"Adsorption of Oxygen on Pt(111) and Its Reactivity to Hydrogen and Carbon Monoxide," D.R. Monroe and R.P. Merrill, Journal of Catalysis, 65, 461 (1980).

"Concentration Profiles in Impregnation of Porous Catalysts: Nickel on Alumina," M. Komiyama, R.P. Merrill and H.F. Harnsberger, Journal of Catalysis, 63, 35 (1980).

"Angularly Resolved Temperature Programmed Decomposition: Nitrogen Emission from the Decomposition of Hydrazine on Ir(111)," H.H. Sawin and R.P. Merrill, J. Chem. Phys., 73, 996 (1980).

"Fourier Analysis of Linear Surface Kinetics in Reactive Molecular Beam Scattering", H.H. Sawin and R.P. Merrill, J. Vac. Sci. and Tech., J. Vac. Sci. Technol., 19(1), (1981).

"Classical Surface Scattering Computations; Rainbows and Energy Exchange," D.R. Dion, J.A. Barker and R.P. Merrill, Surface Science, 95, 15 (1980).

"A Semi-Classical Trajectory-Based Calculation of the Multiple Scattering Problem," A.P. Jauho, M. Cohen, J. Wilkins and R.P. Merrill, to be published in the Proceedings of the Conference on Determination of Surface Structures by LEED," P.M. Marcus and F. Jona, Editors.

"Molecular Orbital Calculations of Atomic Hydrogen Chemisorption on the Beryllium(0001) Surface," G.B. Hoflund and R.P. Merrill, Journal of Physical Chemistry, 85, 2037 (1981).

"Angular Resolved Photoemission from  $\text{NH}_3$  on Ni(110)," K. Jacoby, E.S. Jensen, T.N. Rhodin and R.P. Merrill, Surface Science, 108, 397 (1981).

"Angular Orientation of  $\text{NH}_3$  on Ni(111) by Low Energy Photoelectron Scattering," W.M. Kung, C.H. Li, S.Y. Tang, C.W. Seabury, K. Jacoby, T.N. Rhodin, R.J. Purtell and R.P. Merrill, Phys. Rev. Letters, 47, 931 (1981).

"A Kinetic Study of Hydrazine Decomposition on Ir(111) by Molecular Beam Scattering and Temperature Programmed Decomposition," H.H. Sawin, Ph.D. Thesis Cornell University (1980).

"Ammonia Chemisorption on Ir(111)," R.J. Purtell, Ph.D. Thesis, Cornell University (1980).

"Impregnated Nickel on  $\gamma$  Alumina Catalyst: Catalyst Design and Impregnation," M. Komiyama, Ph.D. Thesis, Cornell University (1980).



Accession No.	7
DTIC TAB	
Unannounced	
Justification	
By	
Distribution/	
Availability Code	
Avail and/or	
Dist Special	

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective of the work supported by this grant was to examine the decomposition of hydrazine on iridium from a molecular point of view. Since this reaction proceeds very rapidly, reaction probabilities near unity, it is impossible to measure intrinsic kinetics by traditional means at pressures near one atmosphere. Accordingly, this work used reactive molecular beam scattering and temperature programmed desorption techniques. A complimentary approach was to use modern spectroscopic techniques to identify the electronic structure and bonding modes of the surface intermediates in the reaction sequence. Auger spectroscopy, X-ray Photoelectron Spectroscopy, and Ultraviolet Photoelectron Spectroscopy were used.

The technological objective of this work was to develop enough understanding of the decomposition mechanism to suggest ways of studying the catalyst de-activation and poisoning and to provide guidance on how to develop more stable catalysts. In order to integrate the findings of our fundamental decomposition studies into this technological objective we also examined the problem of reaction and diffusion in porous catalysts from a molecular view and did some work to identify the mechanisms which control the radial concentration profiles which develop when catalysts are made by aqueous impregnation of porous oxide supports.

Using the combination of reactive molecular beam scattering and temperature programmed desorption it has been possible to determine most of the salient features of the reaction sequence of hydrazine decomposition on the (111) face of iridium. The reaction "lights-off" at 200°K to a reaction probability of 0.95 or greater and stays nearly constant up to 1500°K, confirming the remarkable reactivity suggested by the conventional catalytic work. From 200°K up to 500°K the primary decomposition products are  $\text{NH}_3$  and  $\text{N}_2$ . Above 600°K little  $\text{NH}_3$  is produced.

There are at least three parallel channels for the production of  $\text{NH}_3$  in the reaction sequence. all three are simultaneously evident in the experimental transfer function between 500°K and 600°K. Only two are absorbed at temperatures ca. 300°K where the catalyst used in thruster engines is required to "light-off". One has a time constant of several seconds and a branching ratio of 0.95. The other channel has a time constant of ca. 1 m sec., but since it produces only 5% of the  $\text{NH}_3$  product it could never be studied in technological catalysts using standard catalyst testing procedures.

Catalyst deactivation causes disintegration of the catalyst particles in thruster service. This is caused by imbibation of the liquid hydrazine into the pores of the pellet. If the catalyst does not light off within  $10^{-3}$  sec. there is too much liquid uptake and the pressure build-up within the interior of the catalyst exceeds the tensile strength of the pellet before the liquid can be pumped back out of the catalyst. Clearly, then, it is the 5% branch of the decomposition reaction that is responsible for the  $10^{-3}$  sec. light off, not the main channel which requires several seconds. This is certainly the most significant technological finding of the work. It means that one must study this fast branch to identify the causes of catalyst deactivation and to develop strategies for improving catalyst stability. This will require carefully designed time response studies in the absence of mass transport limitations and will not be possible using steady-state measurements.

Initially, hydrazine adsorbs dissociatively onto the clean iridium surface to produce adsorbed hydrogen atoms and a di-adsorbed di-imide. Adsorption into this state is irreversible and TPD of this species yields  $\text{NH}_3$  and  $\text{N}_2$ . A reversibly adsorbed hydrazine can adsorb onto this di-imide. The decomposition of the di-imide-hydrazine complex to give gas phase  $\text{N}_2$  and two adsorbed  $\text{NH}_3$  comprises one of the decomposition branches, i.e. the slow branch at  $300^\circ\text{K}$ . The fast branch at  $300^\circ\text{K}$  passes through an  $\text{NH}_2$  adsorbed species which adds adsorbed H to give  $\text{NH}_3$  which subsequently desorbs. The third branch results from successive dehydrogenation of a mono-adsorbed di-nitrogen species and subsequent addition of hydrogen to non-adsorbed nitrogen to give a sort of nitrogen analog of adsorbed methyl isocyanide,  $\text{H}_3\text{N}-\text{N}\equiv\text{Ir}$ . This species then decomposes to give gaseous  $\text{NH}_3$  and adsorbed N atoms. This complex reaction sequence has within it fourteen elementary steps. The studies have been able to measure the rate of 13 of these fourteen steps at at least one temperature. Four of the elementary rates have been measured over a sufficiently wide temperature range that both pre-exponentials and activation energies have been determined. The role of surface diffusion is evident in the steps involving adsorbed hydrogen addition and in the slow branch passing through the hydrazine/di-imide complex.

Spectroscopic evidence for  $\text{N}_2\text{H}_4$ ,  $\text{NH}_2$ ,  $\text{NH}_3$  and N surface intermediates has been found. Adsorbed  $\text{NH}_3$  has been characterized most completely.  $\text{NH}_3$  adsorbs through the nitrogen lone pair with the hydrogen triad parallel to the surface. The N-H bonding orbitals are barely shifted by adsorption though the lone pair is stabilized by adsorption. The amount of stabilization of the lone pair on different metals correlates with its chemisorption binding energy. The work function change is very large,  $-3$  eV on a saturated overlayer. This is too large to be attributed only to orientation of the gas phase dipole and implies charge transfer from the lone pair into the iridium metal. The chemisorption binding site is one of the three fold hollows on the (111) surface and the  $\text{NH}_3$  molecule is rotationally oriented by adsorption. There is also a density driven phase transition at ca.  $120^\circ\text{K}$  which nucleates a (2x1) surface structure that produces a strong dispersion in the the energies of the 1e N-H bonding orbitals as two dimensional energy bands are formed.

Ammonia TPD exhibits three desorption states, but no decomposition to Nitrogen when the surface is scrupulously clean of oxygen. These same three peaks are present, with some changes in relative intensity, when hydrazine is decomposed by temperature programming.

In aqueous impregnation it has been demonstrated that one can control the radial concentration profiles of metal as it is deposited on the interior pore walls of a macroscopic support pellet by adjusting the adsorptivity of the species. A model has been developed which adequately predicts changes in the profiles. One can obtain a uniform profile, a profile where most of the metal is deposited near the exterior of the surface of the catalyst pellet, a sub-surface impregnation, or a band of metal may be deposited with the exterior being free of metal and the center of the pellet also being free of metal. The concepts were demonstrated using nickel solutions impregnated into aluminum spheres. Measurements were made using x-ray fluorescence in an electron microprobe.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
AFOSR-TR- 82 - 0206		3. RECIPIENT'S CATALOG NUMBER <i>AD-A114868</i>	
4. TITLE (and Subtitle) Fundamental Studies of the Structure and Chemistry of Solid Surfaces		5. TYPE OF REPORT & PERIOD COVERED Final	
7. AUTHOR(s) Robert P. Merrill		6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Cornell University School of Chemical Engineering Ithac, NY 14853		8. CONTRACT OR GRANT NUMBER(s) AFOSR-80-0103	
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NC Bolling AFB, DC 20332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/A2 <i>Dec. 1980</i>	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 4	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Hydrazine                      Molecular Beam Scattering Iridium                        Temperature Programmed Desorption Catalysis                      Auger Spectroscopy Poisoning                      X-ray Photoelectron Spectroscopy Thruster Engine                Ultraviolet Photoelectron Spectroscopy			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this project was to examine the decomposition of hydrazine on iridium from a molecular point of view. An understanding of the decomposition reaction is critical to the development of catalytic thruster engines which are less prone to catalyst deactivation and poisoning than present devices. The surface techniques employed to follow the reaction included reactive molecular beam scattering, temperature, programmed desorption, Auger spectroscopy, X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy. These			

DD FORM 1473  
1 JAN 73

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Techniques allowed determination of most of the salient features of the reaction sequence of hydrazine decomposition on the (111) face of iridium. At least three parallel channels for the production of  $\text{NH}_3$  were found. Branching ratios and time constants were determined for each of these reactions. The results clearly indicated which reaction mechanism is responsible for thruster "lights-off" as well as indicating a mechanism for catalyst decomposition and break-up.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

DATE  
ILME  
—8